High Power Impulse Magnetron Sputtering of CIGS Thin Films for High Efficiency Thin Film Solar Cells

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In this work $CuIn_{1-x}Ga_xSe_2$ (CIGS) thin films with three different values of *x* (0; 0.28; 1) were prepared by nonreactive sputtering of Cu, In and Ga in HiPIMS (High Power Impulse Magnetron Sputtering) or DC magnetron and subsequently selenized in an Ar+Se atmosphere. Optical emission spectroscopy (OES) was used to monitor some basic plasma parameters during sputtering of metallic precursors. CIGS thin film characteristics were measured using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX) and other techniques.

Keywords: CIGS, HiPIMS, emission spectroscopy, thin films, magnetron sputtering

1 INTRODUCTION

For more than 30 years CIGS solar cells represent the most promising thin film technology for solar energy conversion [1]. The current world record achieved in 2014 by Zentrum Sonnenenergie & Wasserstoff Forsch Baden in Stuttgart is 20.8% [2]. High efficient CIGS devices are usually fabricated by thermal co-evaporation from elemental sources Cu, In, Ga and Se [3], but similar results are possible to achieve by a two-step process which consists of DC sputtering of metallic precursors Cu, In and Ga followed by selenization in Se, Ar + Se or H_2Se atmosphere. In this work we prepared CIGS absorber by High Power Impulse Magnetron Sputtering (HiPIMS) of metallic precursors followed by selenization in Ar + Se atmosphere. The HiPIMS deposition technique has a distinct advantage of producing smoother, denser films of enhanced crystallinity as compared to DC magnetron sputtering. This is due to high energy pulses in a short duty cycle (about 1% of period) which results in a dense plasma with a very high degree of ionization depending on sputtered material [4]. In thin film photovoltaic industry the HiPIMS was successfully used for preparing of ZnO:Al and ITO thin films with improved morphology and damp heat stability [5] and for reactive sputtering of CIGS absorbers with positive effect on overall quantum efficiency [6]. Our attention was focused on comparison of HiPIMS and DC plasma during sputtering of Cu, In and Ga precursors for CIGS absorbing layer depending on Ga/In ratio and their influence on CIGS thin film properties.

2 EXPERIMENTAL DETAILS

CIGS thin films were prepared by two-step process. In the first step, the metallic precursors Cu, In and Ga were sputtered on Mo covered soda-lime glass substrate by HiPIMS or DC magnetron from 2-inch single composite target. Prior deposition the substrate surface was activated by RF plasma (P_{RF} = 100 W, t = 5 min.) in order to achieve better adhesion of sputtered films. Three different targets in sputter down configuration with stoichiometry $Cu_{0.45}In_{0.55}$, $Cu_{0.45}In_{0.40}Ga_{0.15}$, $Cu_{0.45}Ga_{0.55}$ and purity 99.99% were used. The distance between substrate and target was for all experiments 8 cm. The base pressure in the chamber was $1 \cdot 10^{-3}$ Pa and the working pressure during deposition was kept at constant value 1.2 Pa.

The magnetron was operated in 3 different modes: (i) DC mode with an absorbed power of 200 W, (ii) HiPIMS mode with absorbed power 50 W, period 10 ms (f = 100 Hz), pulse time 100 µs (duty cycle 1%) and peak current in the pulse 6 A, (iii) HiPIMS mode with absorbed power 110 W, period 15 ms, pulse time 100 µs (duty cycle 0.67%) and peak current in the pulse 30 A. The deposition time was approximately 10 min for DC prepared samples and 13 respectively 20 min for HiPIMS prepared samples due to expected differences in

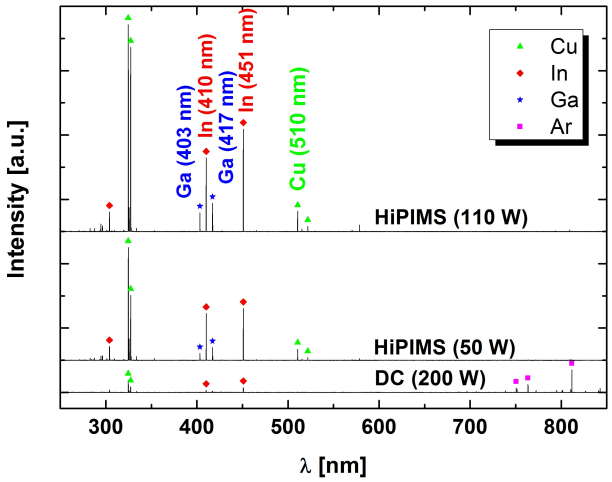

Fig.1. Optical emission spectrum of HiPIMS and DC plasma during sputtering of CuInGa metallic precursors

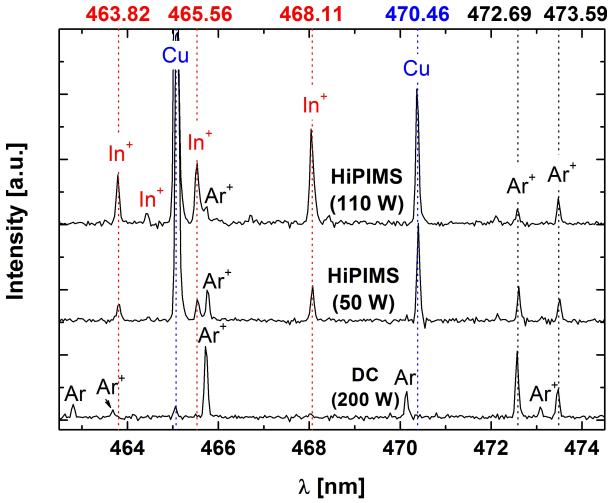

Fig.2. Detail of the same spectrum from Fig. 1; in comparison with previous picture, y-axis with spectral intensity is zoomed 1000x

sputtering rates. The thickness of all CuInGa films was after first step about 1 µm.

In the second step, metallic precursors were selenized in order to form chalcopyrite Cu(In,Ga)Se_2. For selenization a quartz halogen lamp heating system with a solid pure selenium source was used. The selenium was placed in a partially closed graphite container along with the substrate. The container was loaded into a quartz tube and evacuated by a rotary mechanical pump to a base pressure of less than 1 Pa. After that, the quartz tube was filled by 1 atm of argon and graphite container was heated up to 300°C (30 min duration) and 550°C (30 min duration) with ramp 50°C/min. The total selenization time was 70 min. Detailed information about thermal treatment of prepared samples can be found in [7].

Properties of obtained CIGS films were measured by grazing incidence X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

3 RESULTS AND DISCUSSION

3.1 OPT. EMISSION SPECTROSCOPY

During HiPIMS and DC deposition of metallic precursors JY spectrometer TRIAX 550 with CCD detector was used to collect optical emission spectra in the range 200-1000 nm. The optical probe was focused onto area close to magnetron target. Fig. 1 shows a comparison of absolute intensities in plasma emission spectra that were taken during three different sputtering modes. In DC mode intensities of neutral metallic lines are negligibly small compared to both HiPIMS modes even though the average absorbed power in case of DC sputtering was 2 respectively 4 times higher. The peak intensities are completely reversed in the case of Ar lines and whereas in HiPIMS spectrum no Ar lines are visible, in case of DC plasma they dominate in the spectrum. This indicates a significantly larger proportion of metal excitation in the plasma than Ar during the pulse in the case of HiPIMS. Similar results are visible also in Fig. 2 where selected detail close to central wavelength 468 nm is presented. Intensities of neutral Cu lines (blue) and In^+ ion lines (red) significantly drop down with decreasing HiPIMS power and no metallic ions were detected in DC plasma. On the other side only very weak Ar^+ lines were noticed in HiPIMS spectra compared to Ar^+ lines observed in DC mode. The structural changes in sputtering targets resulted in significant differences in measured emission spectra. Similarly as we found before in case of sputtering perovskite $BaSrTiO_3$ thin films [8] ratio of sputtered particles Cu, In and Ga can be controlled by means of optical emission spectroscopy and this ratio can be correlated with final stoichiometry. It was found that ratio of emission spectral line intensities and the ratio of concentrations in the film are approximately proportional for the same geometry setup. This dependence is

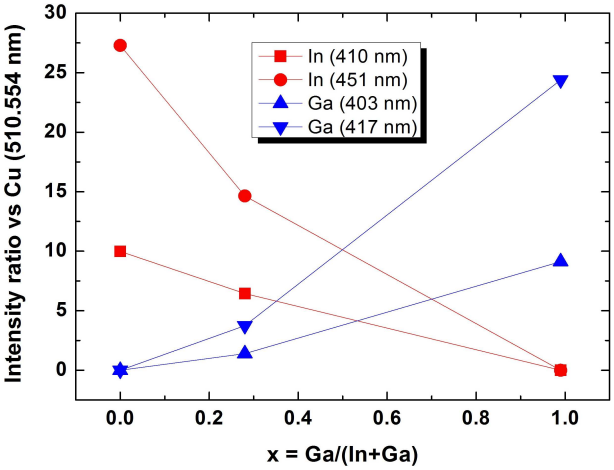

Fig. 3. The spectral intensity ratio of In/Cu and Ga/Cu in DC plasma as a function of structural parameter x in final CIGS thin films measured by EDX

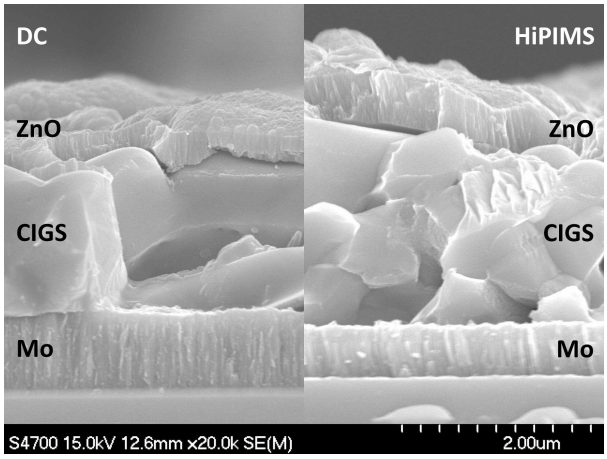

Fig.4. SEM cross-sectional image of CIGS devices with CIGS absorbed layer prepared by DC sputtering (left) and HiPIMS (right)

demonstrated in Fig. 3 where the ratio of intensity of selected In and Ga lines versus intensity of line Cu 510.544 nm is depicted as a function of structural parameter *x*.

3.2 THIN FILM PROPERTIES

XRD patterns of selected HiPIMS prepared $CuIn_{1-x}Ga_xSe_2$ thin films with various x ratios revealed well-formed chalcopyrite crystal structure with lattice parameters in the range a = 5.78 Å, c = 11.56 Å (CIS) and a = 5.59 Å, c = 10.97 Å (CGS). The chemical composition of mixed CIGS thin films measured by EDX was very close to initial Ga/In ratio in the target. Raman spectra measured in the range 100 to 400 cm^{-1} revealed typical chalcopyrite structure with dominate A_1 phonon frequency from 175 cm^{-1} (CIS) to 185 cm^{-1} (CGS). SEM images (see Fig. 4) confirmed very similar grain structure independently of sputtering mode. No significant differences in chemical composition, XRD spectra, or Raman spectra in case of HiPIMS and DC prepared samples were noticed.

4 CONCLUSION

$CuIn_{1-x}Ga_xSe_2$ thin films with various Ga/In ratio were prepared by DC and HiPIMS sputtering of metallic precursors followed by selenization in Ar + Se atmosphere. Although no significant differences between DC and HiPIMS prepared absorbers were noticed, optical emission spectra demonstrated significant changes between HiPIMS and DC plasma during sputtering of Cu, In and Ga particles. It was shown, that chemical composition of precursors films can be controlled by monitoring of selected spectral lines of Cu, In and Ga.

Acknowledgements

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